NANOHYBRID MATERIALS BASED ON CARBON NANOTUBES ENCAPSULATING CATALYTIC NANOPARTICLES: ELABORATION, CHARACTERIZATION & APPLICATIONS

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by

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Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
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CERTIFICATION OF APPROVAL

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BACHELOR OF ENGINEERING (Hons)
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Approved by,

_____
(Dr Moulay Rachid Babaa)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

KHAIRUL ANWAR B MUHAMAD

ABSTRACT

This report basically discusses the research done and understanding of the chosen topic, which is **Nanohybrid Materials Based on Carbon Nanotubes Encapsulating Catalytic Nanoparticules: Elaboration, Characterization & Application**. The aim of this project is to create nanohybrid material that will increase efficiency and performance of the existence material. The pristine Multi-Walled Carbon Nanotubes (MWNT) will be oxidized first with acid nitric through acid treatment. Metal oxide will be encapsulated inside the Multi-Walled Carbon Nanotubes (MWNT) by using hydrothermal route. Characterization techniques such as Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR), Thermo Gravimetric Analysis (TGA), Transmission Electron Microscopy (TEM), and X-Ray Diffraction (XRD) are being used to investigate the structure of the carbon nanotubes. From the characterization results, it is clearly can be seen that after the acid treatment reaction, the tip of the tube is open for Multiwalled nanotubes (MWNT) while it is close for pristine single walled nanotubes (SWNT). Also, from the FTIR result, it is proven that ZnO were introduced or encapsulated inside the MWNT after simple hydrothermal route reaction. Finally, the application of this nanohybrid material will be elaborated.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

A new generation of carbon nanotubes (CNTs) is more and more the focus of the research worldwide. They result from transformation of "regular" CNTs by various ways such as functionalization, doping, substitution, etc. The new nanomaterials thereby created are likely to exhibit new behaviors, specifically regarding properties that pristine CNTs do not possess (reactivity, solubility, magnetism...). [1]

Hybrid CNTs are one example of meta-nanotubes, and consist in CNTs whose the hollow core is fully or partially filled with foreign atoms, molecules or compounds. The inserted material may then exhibit a peculiar behavior with respect to the macroscopic state for several non-exclusive reasons: 1D-dimension preventing electron scattering and enhancing the role of surface atoms, protection from surface adsorption of disturbing molecules by the carbon sheath, anisotropic lattice distortion or creation of new structures due to imposed dimensions, interactions / electron coupling with the surrounding carbon lattice. [1]

In this project, there are 4 major stages:

1) Acid Treatment (Opening CNT)
2) Hydrothermal Route for Multi Walled Carbon Nanotubes (MWNTs)-ZnO nanoparticles synthesis.
3) Catalytic Reaction.
4) Characterization.

Each stage would be explained respectively later in the report.

1.2 PROBLEM STATEMENT

Nowadays, that catalyst being used by the industry is in a bulky form and the life span is short. Thus, this will definitely increase the operation cost. By putting nanoparticules inside carbon nanotubes, it is aim to create a new type of material with new properties that will be proved experimentally better than the existence one, physically, economically and performance wise.

Researchers from time to time have tried to study the underlying physics and considerable work is available in the literature. Therefore, this project will aim to understand the concept and proof the theory that nanohybrid materials can improve the efficiency and performance of existence materials.

1.3 OBJECTIVE AND SCOPE OF STUDY

The aim of the project is to conduct a study which will utilise the experimental and modelling capabilities available at Universiti Teknologi PETRONAS to produce nanohybrid materials.

The main objectives of this research are:

- To elaborate nanohybrid materials by encapsulating catalytic nanoparticles into carbon nanotubes.
- To investigate the applications of nanohybrid materials in petrochemical process namely :
    - Improvement of life span for catalyst
    - Improvement of the performance and efficiency in catalytic reaction

CHAPTER 2

LITERATURE REVIEW

Carbon Nanotubes

The transport of simple and complex fluids in carbon nanotubes (CNTs) is of interest from both fundamental science and the applications points of view. Carbon nanotubes are a convenient material with which to work for several reasons [2]:

1. Carbon nanotubes can be fabricated with diameter ranging from a fraction of a nanometer to several hundreds of nanometers allowing one to conduct experiments with various tube sizes
2. The surface properties of the tubes can be modified thermally and/or chemically to facilitate behaviors ranging from hydrophilic to hydrophobic, allowing one to probe the effect of surface properties on the behavior of the liquids.
3. The walls of the tubes are sufficiently thin to be transparent to light and electrons, allowing one to observe and quantify events that take place inside tube.
4. The tubes can contain high pressure fluids and gases for an extended time even in vacuum environment of the electron microscope.

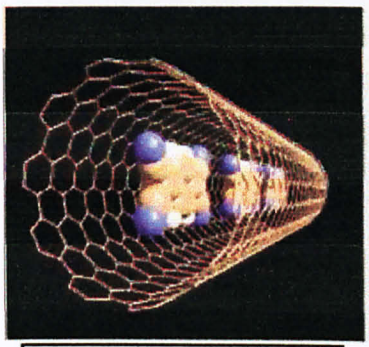


Fig 1. Single walled carbon nanotube encapsulating TCNQ

[Taken from : 4]

Single walled carbon nanotube (SWNT) is the most promising material for molecular electronics because of its unique structural and electronic properties. Molecular electronic is an emerging area in which the goal is using molecular materials as core device components. An advantage of molecular electronics is the small size of the core components, surpassing structures attainable by top-down lithography and could therefore be essential for miniaturization.

Capillarity

Single walled carbon nanotubes (SWNTs) exhibit similar capillarity properties to those exhibited by multiple walled carbon nanotubes (MWNTs). SWNTs previously filled in low yield (ca. 2%) by solution chemistry techniques, can be filled in high yield (up to ca. 50%) by the liquid phase method. [3]

Composition from the KCl-UCl_4 and AgCl-AgBr systems were used to fill SWNTs without causing them significant chemical or thermal damage in the case of the latter, exposure to light or an electron beam resulted in the partial photolytic reduction of SWNT incorporated silver halides to continuous metallic silver 'nanowires' within the capillaries.

It has been demonstrated a simple and reproducible method for the continuous filling of the capillaries of SWNTs in high yield with a variety of materials, thereby showing that these types of nanotubes exhibit similar wetting and capillarity properties to MWNTs. The advantages of using SWNTs over MWNTs:

- The former are relatively much more uniform
- Defect free structures in comparison to the latter and their composite properties will be correspondingly more uniform

Hybrid Carbon Nanotubes

Hybrid nanotubes are CNTs which the inner cavity has been filled with foreign atoms, molecules, or compounds. They are probably the most versatile of the meta-nanotubes and are likely the ones which open the wider research field, both regarding scientific and technological aspects. [1]

Both MWNTs and SWNTs are able to be transformed into hybrid CNTs (noted X@CNT, where X is generally the chemical formulae of the filling material). However, because of the smaller diameters involved in SWNTs as opposed to MWNTs, more specific properties are expected for X@SWNT due to the truly 1D-morphology enforced for the filling materials. The inserted material may exhibit a peculiar behavior (e.g., quantum wire) with respect to the macroscopic state, for several non-exclusive reasons:

- 1D-dimension preventing electron scattering and enhancing the role of surface atoms.
- Protection from surface adsorption of disturbing molecules by the carbon sheath.
- Anisotropic lattice distortion or creation of new structures due to imposed dimensions.
- Interactions / electron coupling with the surrounding carbon lattice.

CNT Based Polymer Composites

Polymers and polymer matrix composite materials are being utilized in an increasing number of industrial applications including transportation, automotive, aerospace, defence, sporting goods, energy and infrastructure sectors. This is due to their high durability, high strength, light weight, design and process flexibility, etc. Polymers such as epoxy (Ruiz et al 1998), thermoplastics (Fiege et al 1999), gels (Gomes et al 1999), as well as poly (methyl methacrylate) (PMMA) (Laurie et al 1998) have been used as the matrix. [7]

The conductivity, strength, elasticity, toughness, and durability of formed composites may all be substantially improved by the addition of nanotubes. The very high aspect ratio of some carbon nanotubes may also enable them to be aligned with one axis of the composite. This high axial electrical conductivity offers the potential for fabricating conducting polymers.

Carbon nanotubes could replace conventional conductive fillers for a range of applications like electrostatic discharge (ESD) and electromagnetic interference (EMI) shielding, and a much lower loading of carbon nanotubes can be used to achieve desired conductivity levels (Grimes et al 2000, 2001).

The effective use of CNTs in composite applications depends on the ability to disperse the CNTs uniformly throughout the matrix without reducing their aspect ratio. Due to the van der Waals attraction, nanotubes are held together as bundles and ropes. Thus they have very low solubility in solvents and tend to remain as entangled agglomerates. To overcome the difficulty of dispersion, mechanical/physical methods such as ultrasonication, high shear mixing, surfactant addition, melt blending and chemical modification through functionalization were used. [8]

Catalytic Reaction: Hydrogenation of Cinnamaldehyde into hydrocinnamaldehyde

Palladium nanoparticules were deposited inside MWNTs via a sample impregnation using an aqueous solution containing a palladium salt. The impregnation method was extremely efficient as no palladium particle located on the outer surface of the tubes was observed. [9]

- Catalytic test
  - The hydrogenation of cinnamaldehyde was carried out in a slurry reactor under atmospheric pressure at 80°C.
  - Add 5 wt.% Pd catalyst to 10 ml of cinnamaldehyde dissolved in 50 ml of dioxane.
  - Continuously fed hydrogen (20 ml min^{-1}) into the reactor via a mass flow controller.
  - Stirr at 500 rpm.
  - A small amount (0.2 ml) of the reacting medium was withdrawn at regular times and analyzed by gas chromatograph.

- Results

  - The catalytic performance was compared with the commercial palladium (5 wt.%) supported on high surface area (800 m^2g^{-1}) activated charcoal catalyst.

  - The conversion was similar over two catalyst , even if the full conversion was faster obtained on the carbon nanotubes, i.e. 100% of conversion after 25 h instead of 27 h for commercial catalyst.

  - In terms of product selectivity, on the carbon nanotubes based catalyst, almost only hydrocinnamaldehyde (HCALD) was observed. The fully hydrogenated product (PP) contributes to about 10%. On the commercial catalyst, both HCALD and PP were observed in an almost equal proportion.

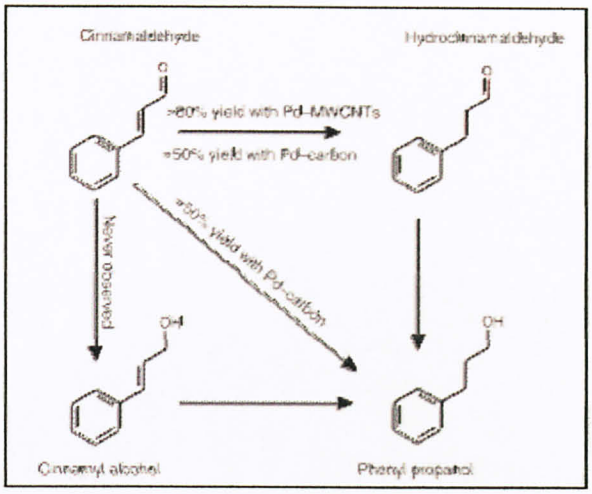


Fig 2: Reaction Pathways in the Hydrogenation of Cinnamaldehyde
[Wildgoose et al., Small 2 (2006) 182-193]

- Discussion

  - The difference in selectivity of both commercial and carbon nanotubes catalyst could be attributed to several factors:

i. The existence of peculiar metal support interaction between the palladium metal crystallites and the carbon nanotubes surface in the inner cavity

i.e. electronic modification through the electron transfer between the metal and the support, which in turn modifies the adsorption and selectivity of the products.

ii. The complete absence of any microporosity as found on the activated charcoal

i.e. this could modify the residence time of the reactants , products and their adsorption properties.

iii. *The low concentration of oxygenated groups on the MWNT surface compared to their high concentration on the activated charcoal*

i.e. influence catalytic selectivity by modifying the adsorption mode of the reactant.

iv. *Presence of residual acidity on activated charcoal*

i.e. modify the hydrogenation pathway leading to a less selective catalyst.

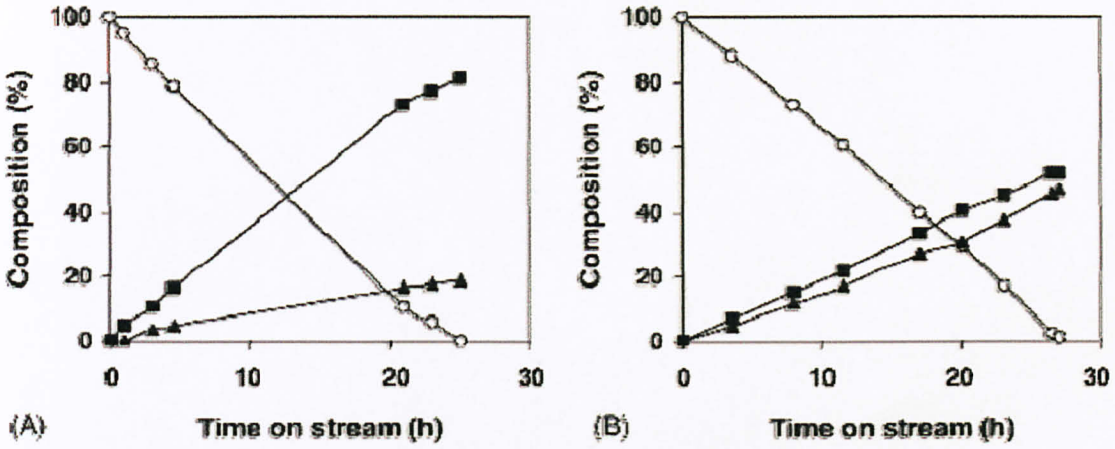


Fig 3: Catalytic activity for the selective hydrogenation of cinnamaldehyde into hydrocinnamaldehyde over

(A) Pd/MWNTand (B) Pd/AC catalysts at 80 8C in a liquid-phase medium:

(○) cinnamaldehyde, (■) hydrocinnamaldehyde, and (▲) 3-phenylpropanol (PP).

Taken from [9]

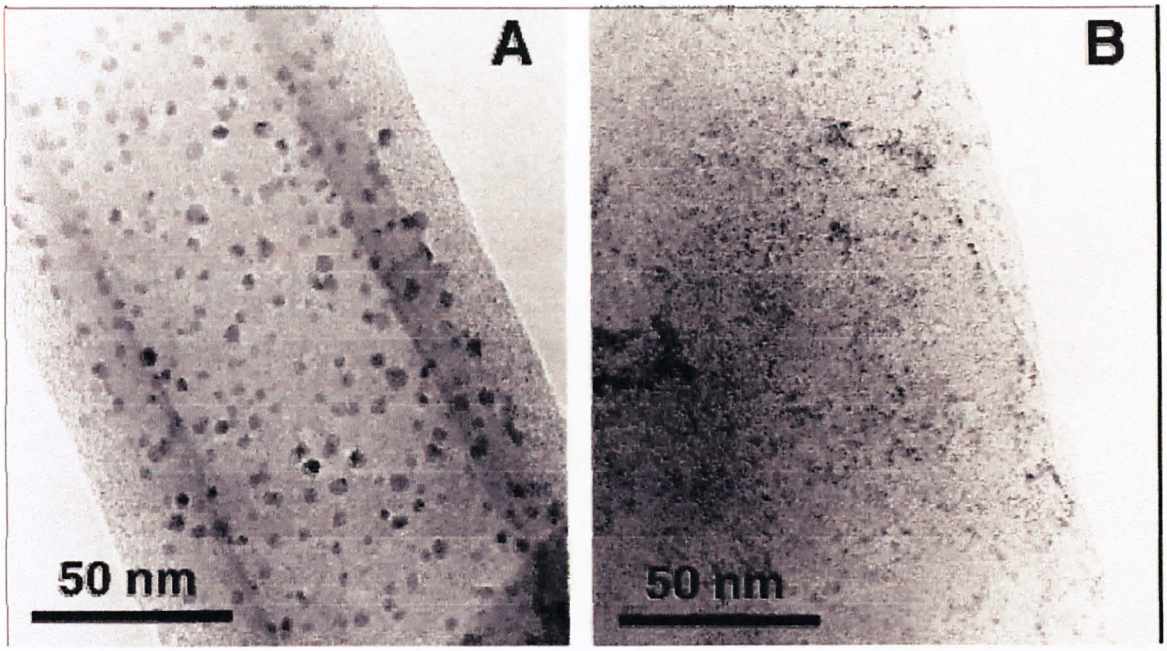


Fig 4 : TEM images of the palladium particles introduced inside the MWNT channel (A) and of a commercial palladium on activated charcoal catalyst (B).
[Taken from 9]

The technique will be used to open carbon nanotubes:

1. Liquid phase

   By using HNO_3 at 69% concentration.

   The temperature will be set at 100 °C for 1 hour duration in reflux condition.

Techniques will be used to characterize encapsulated carbon nanotubes:

1. Transmission Electron Microscopy (TEM)
   - A microscopy technique whereby a beam of electron is transmitted through an ultra thin specimen as they pass through.
   - An image is formed from the interaction of the electrons transmitted through the specimen, which is magnified and focused onto an image device, such as a fluorescent screen, as is common in most TEMs, on layer of photographic film, or to be detected by a sensor such as CCD camera.
   - Allows one to obtain volume-specific information on the nanomaterials having complex morphology or spatial distribution.
   - Enable to access unprecedented information on the microstructural arrangement of individual particles forming the nanowire and its relationship toward the magnetic behavior of those structure.

2. Scanning Electron Microscopy (SEM)

- A type of electron microscope that images the sample surface by scanning it with a high-energy beam of electron in a raster scan pattern.

- The electron interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

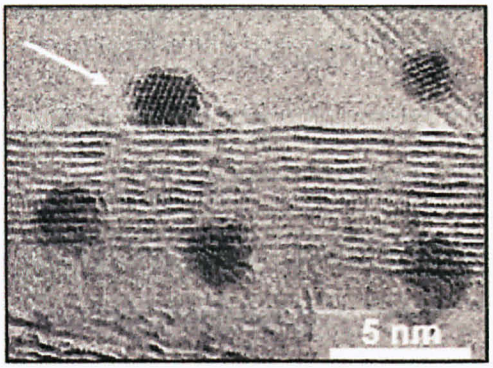


Fig 5 : Example of SEM image
[Bittencourt et al., Surf. Sci. 601 (2007) 2800-2804]

3. X-ray Diffraction (XRD)

- A family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films.

- These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization and wavelength or energy.

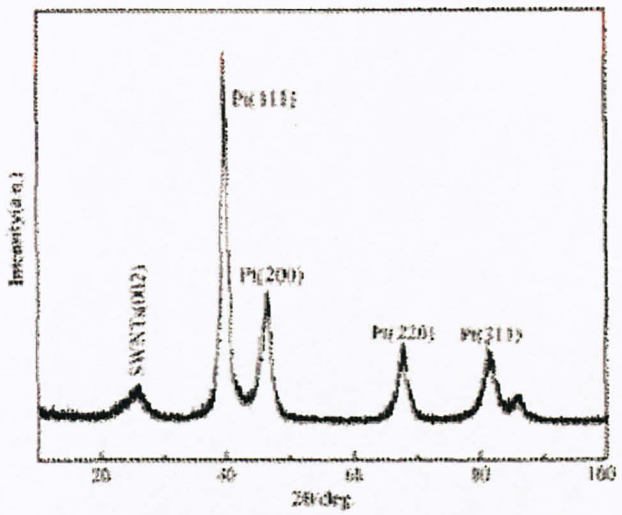


Fig. 5. Powder X-ray diffraction (XRD) pattern of Pt/SWNT composites.

Fig 6 :Example of XRD pattern

[*D.-J. Guo and H.-L. Li, Journal of Power]Sources 160 (2006) 44-49*]

- Single-crystal X-ray diffraction- is a technique used to solve the complete structure of crystalline materials, ranging from simple inorganic solids to complex macromolecules, such as protein.

- Powder diffraction (XRD)- is a technique used to characterize the crystallographic structure, crystalline size (grain size), and preferred orientation in polycrystalline or powdered solid samples.

- Powder diffraction is commonly used to identify unknown substances, by comparing diffraction data against a database maintained by the International Centre for Diffraction Data.

4. Fourier Transform Infrared Spectroscopy (FTIR)

- A measurement technique for collecting infrared spectra. Instead of recording the amount of energy absorbed when the frequency of the infra-red light is varied (monochromator), the IR light is guided through an interferometer. After passing through the sample, the measured signal is the interferogram. Performing a mathematical Fourier transform on this signal results in a spectrum identical to that from conventional (dispersive) infrared spectroscopy.

- Cheaper than conventional spectrometers because building of interferometers is easier than the fabrication of a monochromator. In addition, measurement of a single spectrum is faster for the FTIR technique because the information at all frequencies is collected simultaneously. This allows multiple samples to be collected and averaged together resulting in an improvement in sensitivity. Because of its various advantages, virtually all modern infrared spectrometers are FTIR instruments.

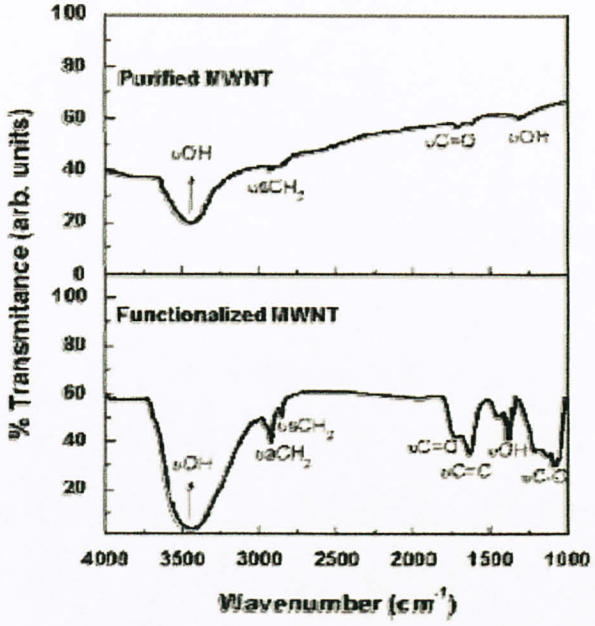


Fig 7 :Example of FTIR characterization
[Taken from 16]

- The FTIR spectra of acid-treated MWNT in the range of 1000.4000 cm−1 is shown in Fig. 7.A broad absorption band at 3437 cm−1 is attributed due to the hydroxyl group _OH [17,18]. This band might have resulted due to water _OH and _H2O [19]and also the −OH functional groups resulting due to the chemical treatment during the purification process and functionalization process, respectively [20].

- Bands at 2927 and 2853 cm−1 are due to asymmetric and symmetric stretching of CH stretching. A small peak at 1734 cm−1 is associated with the C&O stretching of the carboxylic acid (–COOH) group [21]. The peak at 1639 cm−1 is due to C&C stretching of the CNTs [22]. The peak at 1384 cm−1 is due to O–H bending deformation in –COOH.A small peak at 1086 cm−1 is assigned to C–O bond stretching [23] . Thus, the generation of –OH and –COOH groups on CNTs due to functionalization is observed.

5. Thermal-Gravimetric Analysis (TGA)

- Thermal-Gravimetric Analysis or TGA is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted.
- A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required.

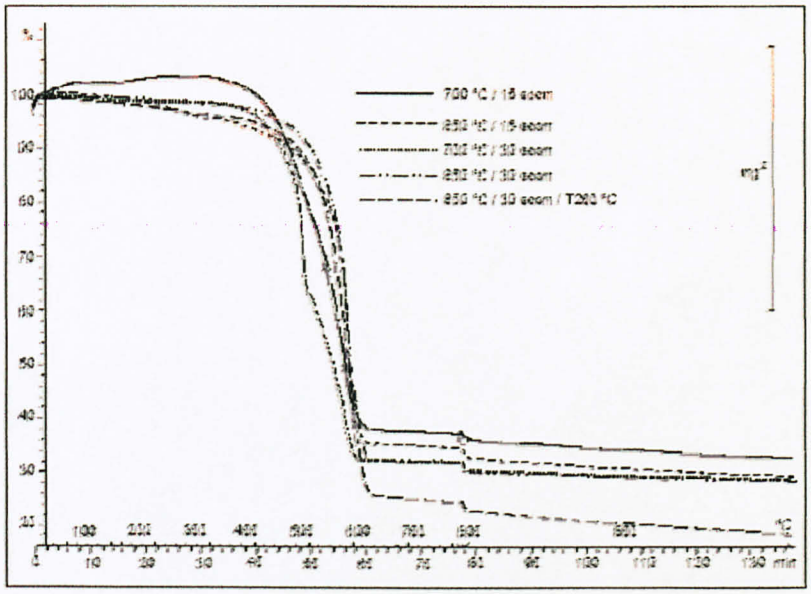


Figure 2 TGA curves of MWNTs synthesized under different temperature and flow rate of C_2H_2

Fig 8 :Example of TGA analysis
[Taken from 11]

- Thermal-Gravimetric analysis (TGA) is a useful technique to understand the purity and thermal stability of CNTs [12]. The impurities presents in the as-grown CNTs as amorphous carbon and defected outer layers are oxidized by thermal treatment in oxidizing atmosphere. The TGA curves showed that the thermal stability and yield of CNTs are vary due to the reaction temperature and flow rate of precursor. Thus, in this work, the TG curves of CNTs samples provide significant information to select the optimum experimental conditions for the synthesis of CNTs [11].

- The TGA curves of MWNTs are shown in Figure 2. All of the samples showed a similar oxidation behavior with single step degradation. Weight loss in the region

  corresponding to CNT oxidation is used to determine the CNT quantity in the samples and hence infer the CNT purity and yield [12], literatures suggest [13, 14, 15] that the weight loss between 450 and 700 °C is specifically due to MWNT

  oxidation.

- During the initial heat treatment, all samples showed a slight mass loss due to the presence of amorphous carbon on the MWNT walls [8]. The MWNTs produced at 700 °C showed 63.31 % weight lost, while the MWNTs obtained at 850 °C has lower weight loss at 61.68 %, this indicated that the purity of the latter sample is lower. Therefore, reaction temperature of 700 °C is more suitable to synthesis MWNTs using supported catalyst of Co/Fe.

Filling materials can be inserted as a solid, a liquid or a vapor, either following in-situ or ex-situ routes. Examples for successful synthesis of hybrid SWNTs via in-situ routes are very seldom, due to the intrinsic constrains associated with the main methods for SWNT synthesis. Ex-situ routes are therefore extensively used. [1]

SWNTs usually require to be opened prior to filling, unless naturally open nanotubes are used. Opening nanotubes is achieved by gas phase or liquid phase oxidation.

EX-SITU SYNTHESIS

There are 3 routes for ***EX-SITU*** synthesis:

Gas Route

- Putting in contact both the previously opened nanotubes and the vapour of material to insert in them.

Liquid Route

- Suspension method

Filling with nanoparticules.

- Solution method (quite similar to suspension method)

Putting in contact a concentrated solution of desired materials with the nanotubes to fill in open air or saturated atmosphere, at room or reflux temperature, possibly assisted by sonication.

- Melting method

If the molting material is not oxidizing towards carbon hence making an opening step necessary on one hand. In some cases, post-treatment is needed. The latter is actually, due to the necessity to deal with material whose melting temperature is below 1000 – 1200 °C and whose surface tension at molten state is below 100 – 200 mN/m.

Single Step Route

- Use solutions of halides ($FeCl_3$, $MoCl_5$, I) in chloroform subsequently irradiated wit UV at room temperature.[1]
- Chlorine moieties are thereby created at least from partial dissociation of $CHCl_3$, which are able to attack the SWNTs, allowing the filling to proceed from the dissolved material. [1]

IN-SITU SYNTHESIS

In contrast to the catalytic decomposition of hydrocarbons on small metal particles, where carbon nanotubes are generally formed together with non-tubular filaments and tubes coated by pyrolytic carbon, this new catalyst method allows the production in situ of SWNTs and MWNTs in a composite powder

A metal oxide nanocomposite powder is prepared by selective reduction in hydrogen of oxide solid solution. This powder is made of oxide grains containing metal particles
with a diameter less than 10 nm. The main part of the particles is located inside the oxide grains but some are found also at the surface. By reducing the powder in a hydrogen–hydrocarbon gas mixture, it is expected that these small particles will be active at an adequate size for the catalytic growth of nanotubes.[6]

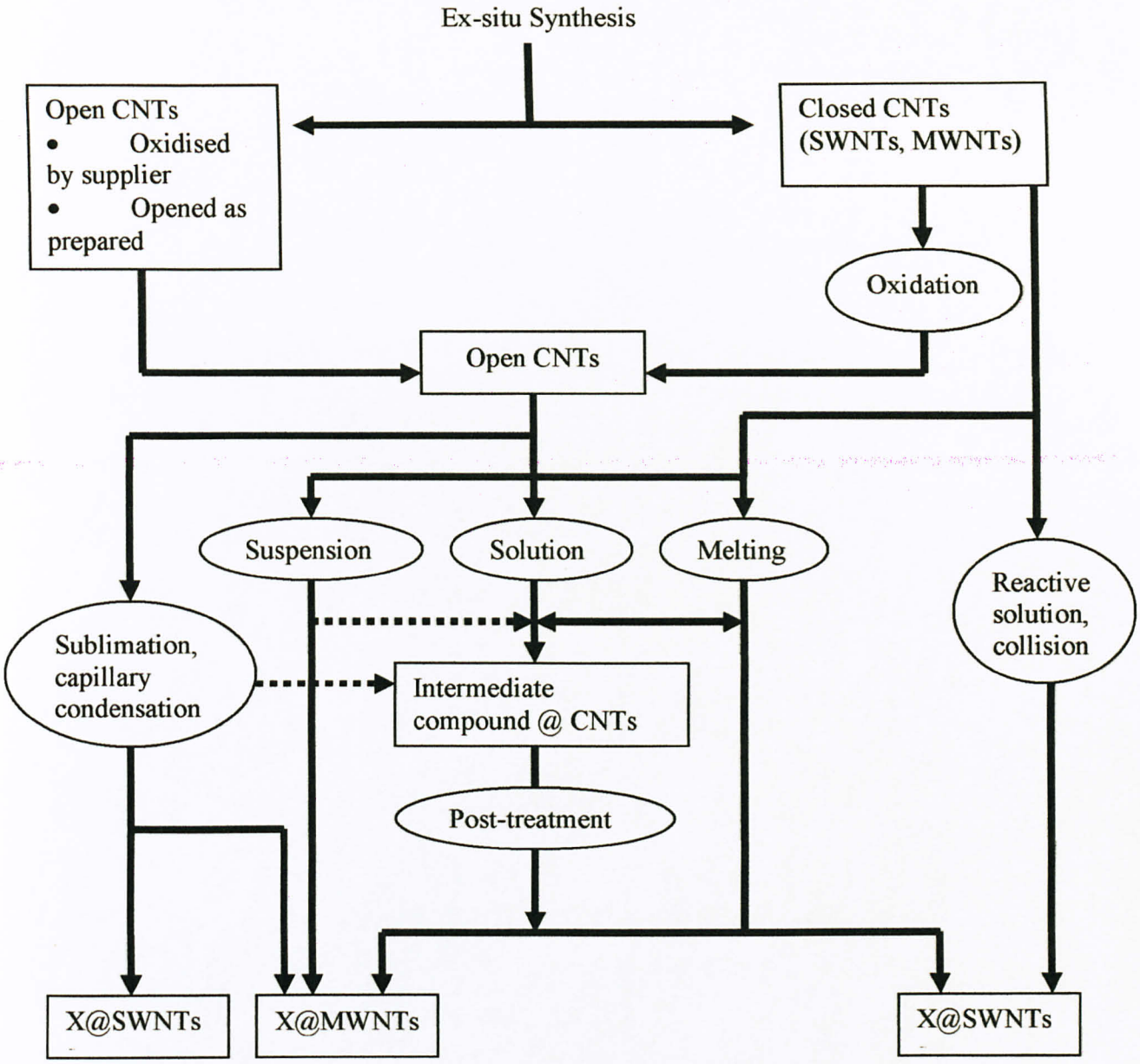


Fig.9. The various ways and steps able to used for ex-situ synthesis of hybrid SWNTs and MWNTs. Rectangle are for materials, ovals are for treatments. Solid lines are preferred paths. *From [1]*

Application

Benzene Hydrogenation

Benzene hydrogenation reaction was applied to evaluate the catalytic activity of hybrid materials. The reaction was carried out in a micro-reactor under atmospheric pressure. Hydrogen gas was employed as reductant and carrier gas. The hydrogen flow was 40 mL·min 1.100 mg catalyst was loaded into micro-reactor and reduced in-situ at 400 _C for two hours before the reaction was performed. After reduction, 1 L benzene was injected into the reactor every time. The product and reactant were analyzed by an on-line SP-6800 gas chromatograph equipped with TCD detector [32].

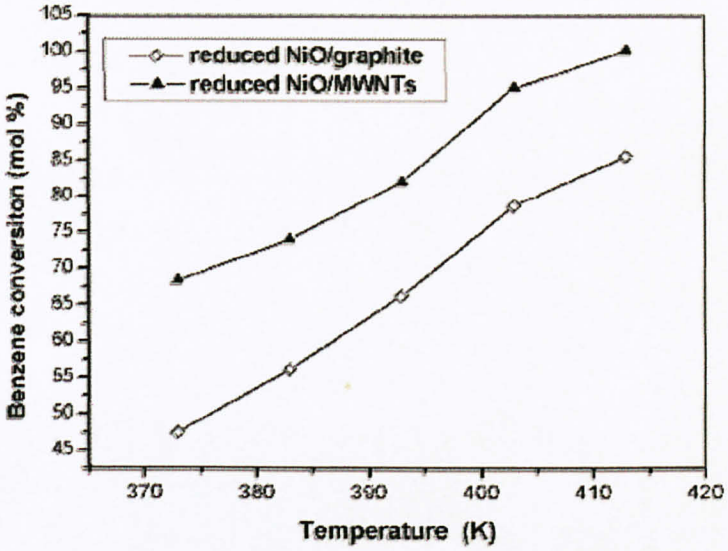


Fig 10 : Catalytic performance of hydrogenated NiO/MWNTs and NiO/graphite for benzene hydrogenation to cyclohexane at different temperature.
[Taken from 32]

Catalytic performance of reduced NiO/MWNTs nanocomposite was carried out by benzene hydrogenation to cyclohexane.

As shown in Fig. 10, benzene conversion is up to 68.3% at 373 K and the conversion is up to 100% at 413 K for hydrogenated NiO/MWNTs sample. Therefore, NiO/ MWNTs hybrid materials present good catalytic performance for benzene hydrogenation to cyclohexane. As a control, NiO/graphite composite was prepared by the same procedure as NiO/MWNTs and its benzene hydrogenation performance was detected under the same condition.

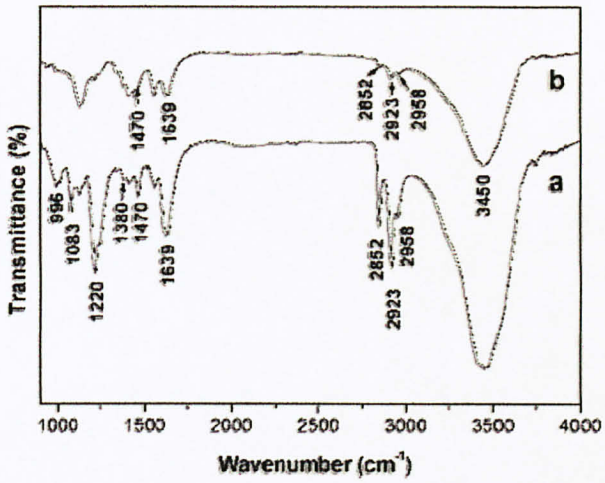


Fig 11 : FT-IR spectrum of (a) SDS; (b) MWNTs-SDS composites.

[Taken from 32]

Comparison two curves in Fig. 11, it is clear that the catalytic activity of reduced NiO/MWNTs is far higher than that of reduced NiO/graphite. A possible explanation could be that MWNTs possesses specific adsorption properties when compared to graphite, and the high conductivity of MWNT might promote hydrogen spillover transport to the active Ni sites, and thus favorable for increasing the benzene hydrogenation reaction rates.[32]

CHAPTER 3

METHODOLOGY

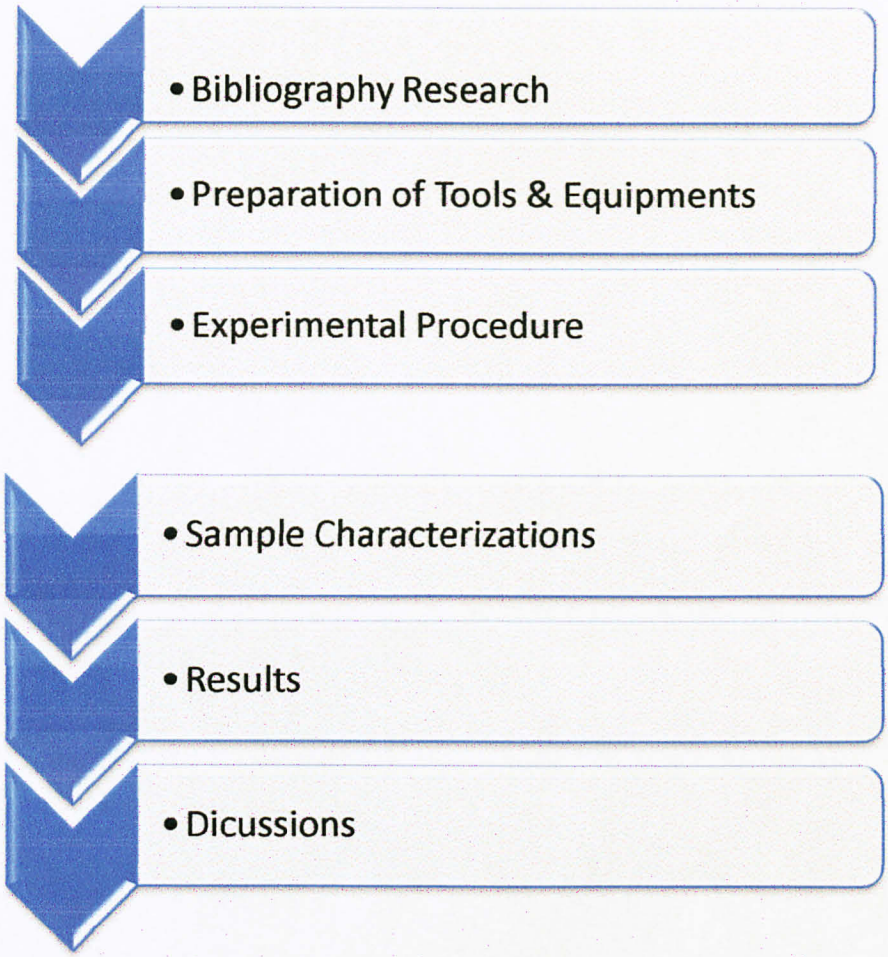
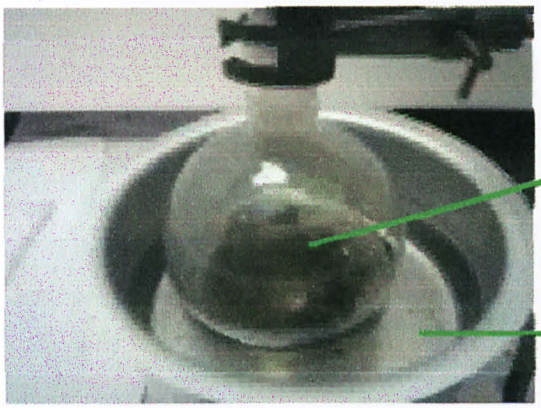


Fig 12: Methodology

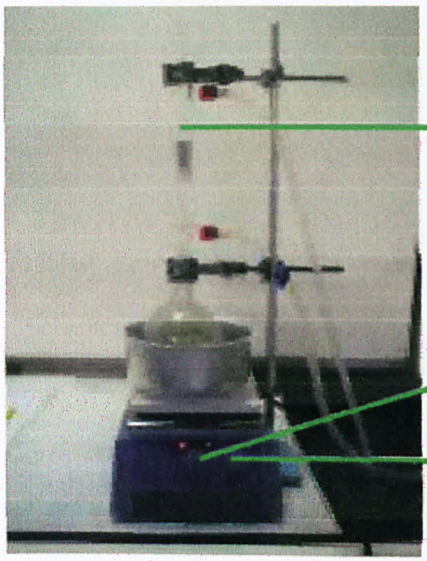
Experimental Works

1. Oxidation of Multi Walled Nanotubes



40 mg of MWNT
+
100 ml of nitric acid 69%

silicon oil



At reflux condition

Temperature at 100 °C

Stirring

For 1 hour 30 minutes

Vacuum filtration and rinsed with distilled water until reaching pH natural.

Dried at temperature 100 °C inside oven

Characterization Test

Fig 13: Experimental works for oxidation of MWNT

2. Hydrothermal Route- Synthesis of MWNT-ZnO nanoparticles

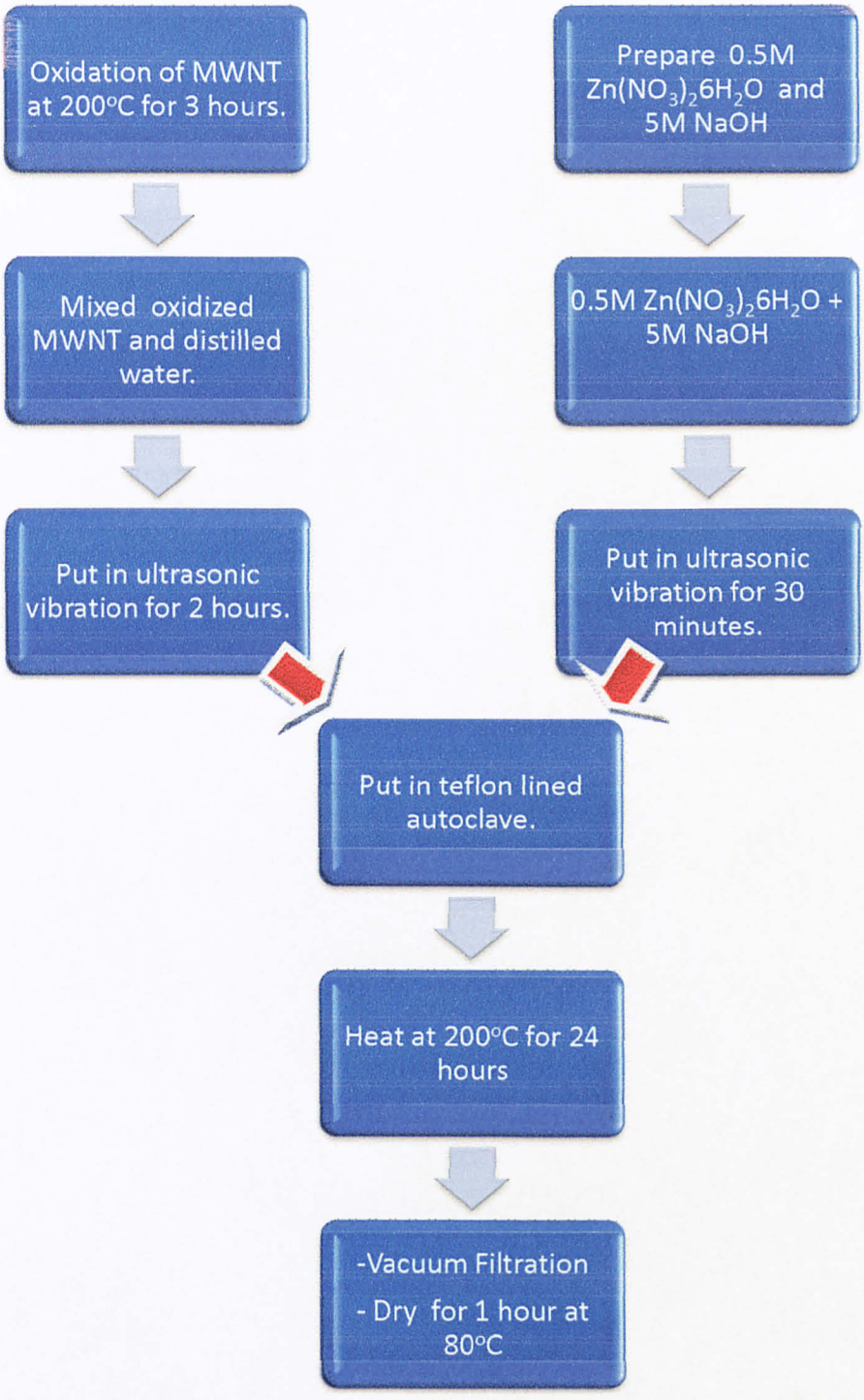


Fig 14: Experimental works for synthesis of MWNT-ZnO nanoparticles

I. Synthesis of Zinc Oxide Nanoparticles

ZnO nanoparticles were synthesized by a simple hydrothermal route. The starting materials used for the synthesis were zinc nitrate hexahydrate, Zn(NO3)2 .6H2O and sodium hydroxide (NaOH). Experimental details are as follows:

First, 0.5 M of Zn(NO3)2 .6H2O and 5 M of NaOH solutions were prepared in distilled water. Next, NaOH solutions was slowly added to Zn(NO3)2 .6H2O under manual stirring followed by sonification for 30 minutes to obtain homogenous solution.

II. Oxidation of MWNT

The oxidized MWNT from the acid treatment functionalization were re-oxidized again. This is to make sure that the tip of the tube really open since the purpose of this project is to encapsulate nanoparticles inside MWNT. Experimental details are as follows:

First, MWNT were put inside oven at 200 °C for 3 hours by using oxidation in air technique. Then, MWNT were mixed with distilled water and followed by sonification for 1 hours or until the solution became black. This step is just to break the solution into small particles or to get homogenous solution.

III. Synthesis of MWNT-ZnO nanoparticles

To proceed with this step, mixed final product of step 1 and step 2 inside Teflon lined autoclave.

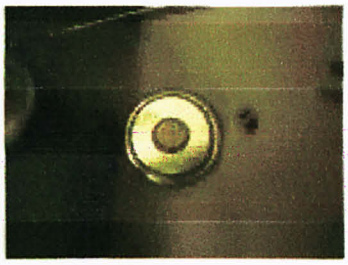
Then, the autoclave was sealed and put inside oven at 200 °C for 24 hours. It was then allowed to cool down at room temperature naturally.

Next, the precipitate were filtered, washed with distilled water to remove the soluble nitrates and with ethanol to reduce agglomeration.

Finally, the precipitate were dried for 1 hour at 80 °C.

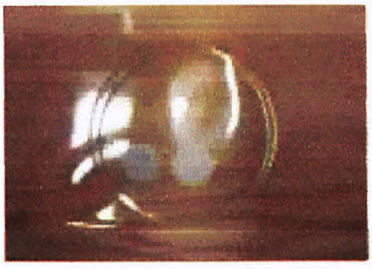
3. Characterization for FTIR

1 mg MWNT
+
299 mg KBr

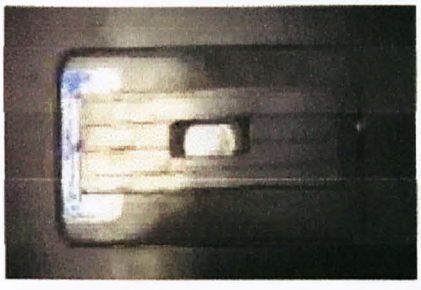


Put inside protuberance

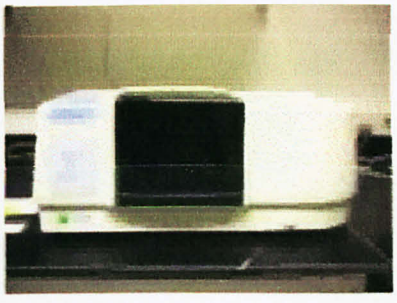
Apply pressure with hand press



Sample in pellet form



Place in disk holder



Ready for characterization

Fig 15: Characterization for FTIR

CHAPTER 4

RESULTS & DISCUSSIONS

Characterization

1. Fourier Transform Infrared (FTIR)

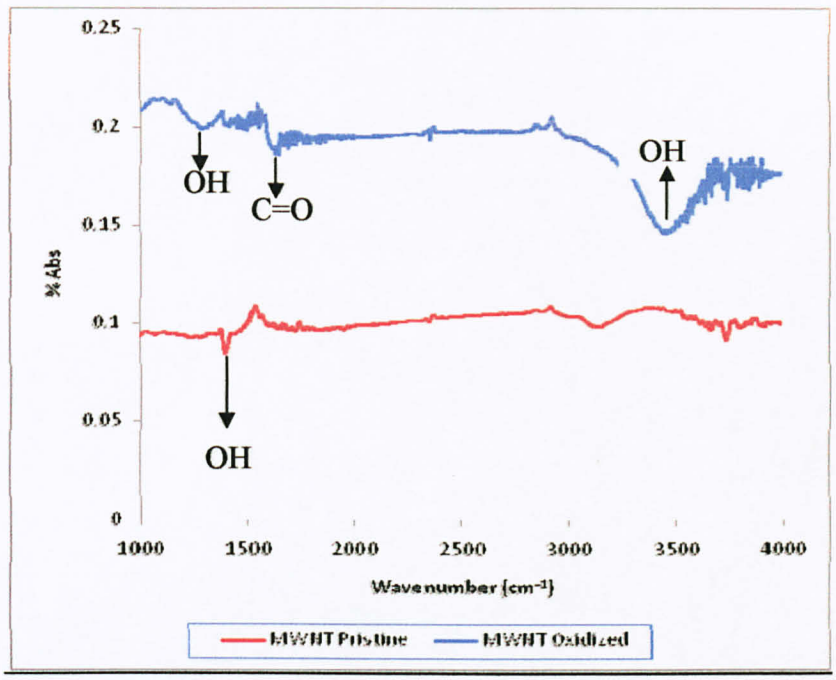


Figure 16: FTIR for pristine MWNT and oxidized MWNT.

To analyze the chemical structure on of the Multiwalled nanotubes, FTIR analysis was carried out. Figure 16 shows the FTIR of pristine MWNT and oxidized MWNT (acid treated).

For Pristine MWNT (red graph), the absorption peak at 1480 cm^{-1} is attributed to the hydroxyl group (-OH).

For acid treated MWNT (blue graph), a broad adsorption peaks at 1380 cm^{-1} and 3480 cm^{-1} are attributed due to hydroxyl group (-OH). This is due to the acid treatment during functionalization and purification process. The peak at 1630 cm^{-1} is associated with the C=O stretching of the carboxylic acid (-COOH). Bands at 2927 cm^{-1} and 2853 cm^{-1} are due to asymmetric and symmetric stretching of CH stretching.

A small peak at 1734 cm^{-1} is associated with the C=O stretching of the carboxylic acid (–COOH) group. The peak at 1639 cm^{-1} is due to C=C stretching of the MWNT . The peak at 1384 cm^{-1} is due to O–H bending deformation in –COOH.A small peak at 1086 cm^{-1} is assigned to C–O bond stretching Thus, the generation of -OH and -COOH group on the MWNT due to functionalization is observed.

Hydroxyl (-OH) group are both observed in FTIR of pristine MWNT and Oxidized MWNT. The adsorption intensity of hydroxyl group obviously increases after the functionalization process. The occurrence of hydroxyl group (-OH) on pristine MWNT may come from lattice water, H_2O [25].

2. Thermal-Gravimetric Analysis (TGA)

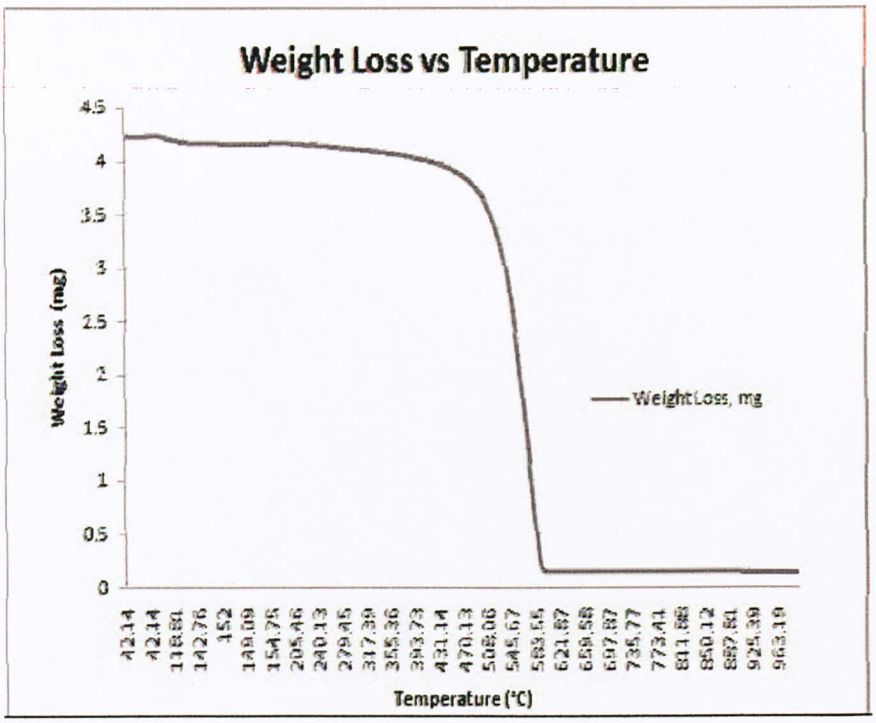


Figure 17 : Thermo Gravimetric Analysis of purified MWNT

Thermal-Gravimetric Analysis is a useful technique to understand the purity and thermal stability of CNT [24].

The impurities presents in the as-grown CNT as amorphous carbon and defected outer layers are oxidized by thermal treatment in oxidizing atmosphere. Weight loss in the region corresponding to MWNT oxidation is used to determine the MWNT quantity in the samples and hence infer the MWNT purity and yield [24] , literature suggest [26,27,28] that the weight loss between 450 to 700 ^{o}C is specifically due to oxidation of MWNT.

During the initial heat treatment, a slight mass loss is due to the presence amorphous on the MWNT walls [28]. The greater the weight loss, the more purified the MWNT. From TGA graph, it is obvious that MWNT can withstand temperature until 1000 ^{o}C. Final residual weights of ~ 5% were obtained for purified MWNT, revealing a purity of about ~ 95% for the purified sample

3. Transmission Electron Microscopic (TEM)

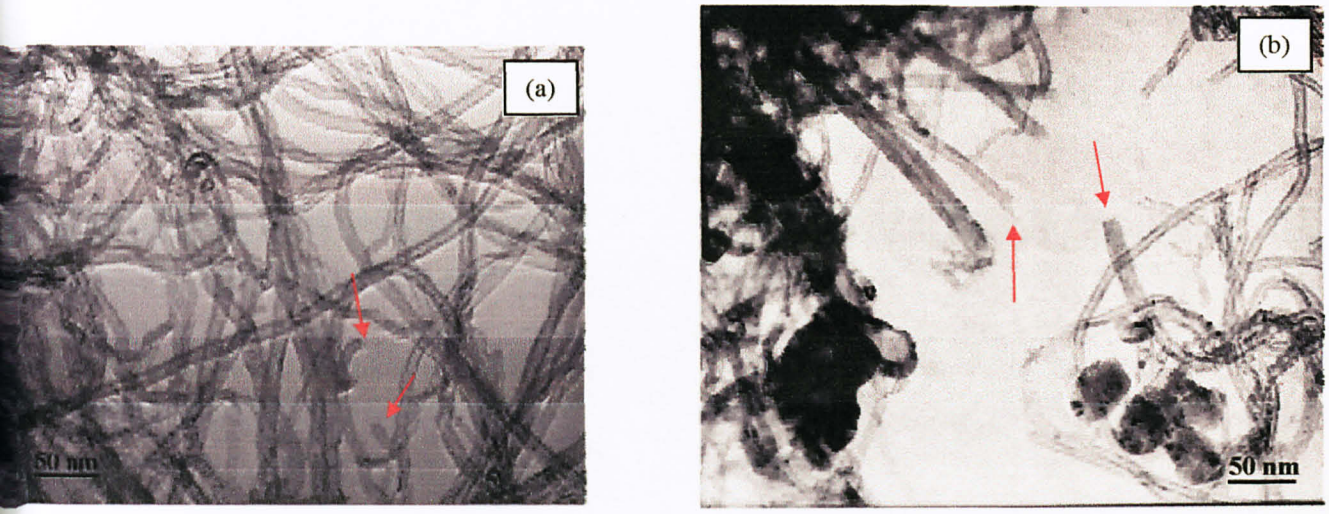


Figure 18 : Transmission Electron Microscopic (TEM) images for : (a) Pristine MWNT
(b) Oxidized MWNT

Figure 18 above shows the (a) pristine MWNT and (b) oxidized MWNT. The opening of MWNT by using acid treatment is proven with TEM image.

Figure 18 (a) shows that at the end of the tip of MWNT are close as shown by the red arrows respectively. It also can be noticed that there is no agglomeration.

However, after acid treatment for 1 hour 30 minutes, the image of 18 (b) shows that at the end of MWNT's tip is open. This is the evidence that by using acid treatment, the opening process of MWNT is happening. In addition, it might be noticed that after functionalization process, the oxidized-MWNT were shortened and debundled. This is because of the harsh process broke shape and size of MWNT during the functionalization [31].

4. X-Ray Diffraction (XRD)

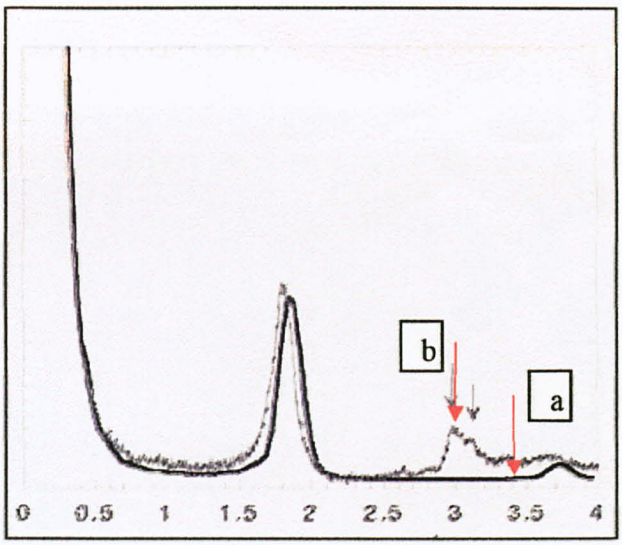


Figure 19 : X-Ray Diffraction results for : (a) Pristine MWNT (b) Oxidized MWNT

Figure above shows X-ray diffraction patterns of (a) Pristine MWNT and (b) Oxidized MWNT. The purpose of this characterization is to show the crystalline structure of MWNT.

As mention in the literature [29], the diffraction peaks of pristine MWNT at 1.9 and 3.55 corresponding to (002) and (004) reflection planes (interlayer spacing between adjacent graphite layer), respectively.

After acid treatment of pristine MWNT the in-plane diffraction peaks of carboxylated MWNTs became significantly broad, while the out-of-plane diffraction peak (002) were maintained at the position similar to the pristine MWNTs. The higher ordered diffraction peak of (004) might merge with weaker and broader peak (102).

For all specimens, the XRD patterns indicate the persistence of the main reflection of the original CNT, at 1.9 and 3.55, assigned to the (002) and (004) reflections of the host lattice [31]. Therefore, the structure of cylindrical concentric carbon layers is preserved but at the same time encapsulated with ZnO nanoparticles. Only the surface is modified.

These results suggested that the carboxylation of MWNTs made some defects on their surfaces, and caused the partial disordering of in-plane reflection planes. As a result, the carboxylated MWNTs were debundled. Debundling of the MWNT chains via carboxylation derives the reduction of crystalline domain size, and the corresponding diffraction peaks are weakened and broadened as referred in a literature [30]. The changes of XRD patterns after acid treatment showed that debundling of MWNT chains and carboxylation on the MWNT surfaces mainly disordered the in-plane orderings.

CHAPTER 5

CONCLUSIONS & RECOMMENDATIONS

5.1 CONCLUSIONS

In conclusion, functionalizations of mutli-walled carbon nanotubes were obtained using acid treatment process. Uniform and highly dispersed zinc oxide nanoparticles encapsulated with MWNT were obtained using hydrothermal route. The results in FTIR, XRD, TGA and TEM confirmed that the MWNT being oxidized.

Oxidized MWNTs were prepared by well-known acid treatment method and structurally and thermally characterized. The use of aqueous nitric acid solution without sulfuric acid was suitable to reduce the damage on MWNT surface. The MWNT chains were seriously shortened in the harsh condition of HNO3/H2SO4 acid mixture solution. The introduction of carboxylic acid groups to MWNTs was somewhat influenced by acid concentration and species, but the prolonged treatment did not improve the further carboxylation on MWNTs.

The surface structure of MWNTs was noticeably changed by the carboxylic acid groups functionalized on the MWNT surface. While the interlayered ordering in a MWNT was maintained after acid treatment, the in-plane orderings were significantly changed due to disordering of the surface structure deduced from the carboxylic acid modification on the MWNT surface.

Among the various kinds of carbon nanotubes derivatives that can be designed and currently prepared, hybrid nanotubes was shown to be probably the most important one for the future development of carbon nanotubes, specifically single-walled. Though progresses and prospects are still necessary regarding synthesis in order to improve filling rates, material variety and quality, and procedures, strong efforts should be made regarding property measurements, theory and modeling.

A lot of work is actually still to be made in the latter fields in order to ascertain the possibilities and limitations of hybrid carbon nanotubes. Based on the fact that peculiar behaviors for the encapsulated materials have already been revealed, it is likely that peculiars properties of the whole hybrid nanomaterials (specifically hybrid SWNTs) will be discovered in a close future.

5.2 RECOMMENDATIONS

Many improvements can be made to make this project become more efficient and effective. This may involve a lot of people from different departments that will contribute directly or indirectly such as:

Experimental wise:

1) If the time is not a limit, the MWNT should be encapsulated with different metals and the results are compare as which one is the most potential to be commercialized.
2) In future, a concern should arise in minimizing the use of expensive metals.
3) Although raw carbon nanotubes have not shown severe adverse effects on health, safety or the environment, more research projects about minimizing the exposure to risks should be conducted.

Facilities wise:

1) Place students request chemical as the important task that the lab executive have to fulfill before the semester start so that student will not loose time waiting for the chemicals requested.
2) All equipments must be undergone details check-up during the semester break so that it would not affect the student progress of work.
3) All the 'under maintenance' equipment must be establish so that student can find others solution ahead.

CHAPTER 5

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